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A simple, rapid and sensitive method based on modified multiwalled carbon nanotube for preconcentration and determination of lead ions in aqueous media in natural pHs



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Abstract In this study, multiwalled carbon nanotube (MWCNT) was modified by the pyridine group using a silane agent and characterized by infrared spectroscopy (IR), thermal analysis (TG/DTA), and elemental analysis (CHN) and scanning electron microscopy (SEM). The application of this sorbent was investigated in determination of lead ions in aqueous samples, using flame atomic absorption spectrometry (FAAS). Through this study, different parameters such as pH and sample flow rate on adsorption process and eluent concentration, volume and flow rate were optimized. The limit of detection (LOD), the relative standard deviation and the recovery of the method were 2 ng mL^{-1} , 1.3% and 99.7%, respectively. Two standard reference materials (NIST 1571 and NIST 1572) were used to verify accuracy of this method. Finally, the sorbent was successfully applied for extraction and determination of low levels of Pb(II) ions in aqueous samples.

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1. Introduction

Determination of trace heavy metals in the environment samples is attracting more attention as heavy metal ions may be accumulated in the human body over a long period of time before they reach to critical level of concentration in certain tissues and the clinical symptoms of the poisoning be observed (Chubar et al., 2003). On the other hand, since it is proved that lead ions cause serious hematological damage, brain damage,

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anemia and kidney malfunctioning, a high sensitive and accurate method is demanded (Dietrich et al., 1990; Goldstein, 1990).

Many instruments such as potentiometric stripping analysis (Coco et al., 1999), FAAS (Tarley et al., 2004), ETAAS (Naseri et al., 2008), fluorescence spectrometry (Evans et al., 2004) and inductively coupled plasma optical emission spectrometry (ICP OES) (Umashank et al., 2002) have been used for the determination of lead ions. Among these instruments, FAAS is the most common technique and have several advantages, including ease of operation and being inexpensive (Soylak et al., 2003). However, this method does not have enough sensitivity for determination of lead ions in natural samples since the lead(II) concentration in these samples is too low. Furthermore, due to the numbers of interferences in complex matrixes of natural samples, a preconcentration step is needed (Tuzen et al., 2008a,b). In this regard, large numbers of sorbents such as Amberlite XAD-4 (Liu et al., 2007), polyurethane foam (Mahmoud et al., 2010), magnetic nanoparticles, TiO_2 (Zheng et al., 2006), alumina and multiwalled carbon nanotube (Duran et al., 2009; Tuzen et al., 2008a,b; Tuzen and Soyak, 2007) have been developed for preconcentration of heavy metals prior to their determination by FAAS. Among these sorbents, multiwalled carbon nanotubes have attracted more attention due to their high thermal and mechanical stability and also being stable in both acidic and alkaline pHs (Ebrahimzadeh et al., 2013). In spite of all fabulous properties of MWCNT, their applications in the absence of surface modifications and functionalization are limited.

In this report, carbon nanotubes were modified by pyridine and used as a novel sorbent for extraction and preconcentration of Pb(II) ions. Various parameters such as sample pH, sample flow rate, eluent type and concentration were optimized. The method was verified using standard reference materials and finally was applied for determination of Pb(II) ions in aqueous samples.

2. Experimental

2.1. Material and reagents

All chemicals were of analytical reagent grade and were used without further purification. HCl , HNO_3 , $\text{Na}_3\text{C}_3\text{H}_5\text{O}(\text{CO}_2)_3$, Na_2HPO_4 , NaH_2PO_4 , CH_3COOH , thiourea, oxalylchloride, triethylamine, 3-aminopropyl triethoxysilane and 4-pyridine carboxylic acid were purchased from Merck Company (Darmstadt, Germany). Carboxylic acid modified MWCNTs, 10–40 nm in diameters, 1–25 μm in length, were purchased from Neutrino Company (Tehran, Iran). Standard stock solution of Pb(II) ions (1000 mg L^{-1}) was obtained from Aldrich (Dorset, UK). The working standard solutions were prepared by appropriate dilution of the stock solution with deionized water and pH adjustments were performed with the appropriate buffer solutions. To adjust pH of solutions to pH of 1–4, a mixture of $\text{Na}_3\text{C}_3\text{H}_5\text{O}(\text{CO}_2)_3/\text{HCl}$ (trisodium citrate/hydrochloric acid) was used. A solution of $\text{CH}_3\text{COOH}/\text{NaCH}_3\text{COO}$ was used to adjust pH values to the range of 4–6 while a buffer solution containing $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$ was used for pH values to the range of 6–9. All the required solutions were prepared using deionized water provided by a Milli-Q (Millipore, Bedford, MA, USA) purification system. Two certified leaf reference materials (NIST 1571

(Orchard Leaves) and NIST 1572 (Citrus leaves)) which used for method validation were obtained from National Institute of Standards and Technology.

2.2. Preparation of pyridine functionalizing agent

Pyridine-functionalizing agent (N-(3-(triethoxysilyl)propyl)isonicotinamide, TPI) was synthesized according to our previously reported procedure (Sadeghi et al., 2012). For this purpose, in a 250 mL two-neck round-bottom flask, equipped with a magnetic stir bar and a reflux condenser, 4-pyridine-carboxylic acid (2.0 g) was suspended in 100 mL of dry dichloromethane under nitrogen atmosphere. Then oxalylchloride (5 mL) was added from a dropping funnel in ice bath and the mixture was stirred overnight. The dichloromethane was removed under reduced pressure, and the residue was suspended again in 100 mL of dry dichloromethane. After addition of triethylamine (7 mL) to reaction mixture, 3-aminopropyltriethoxysilane (4.0 g) was slowly added. The reaction mixture was stirred at room temperature for further 4 h, and then the mixture was suspended in water to remove impurities. Finally, the organic phase separated and the solvent was removed under reduced pressure to obtain brownish viscose oil. The synthesis of TPI was confirmed by ^1H NMR [0.61 ppm (t, 2H), 1.25 ppm (t, 9H), 1.65 ppm (m, 2H), 3.36 ppm (m, 2H), 3.72 ppm (q, 6H), 7.24 ppm (s, 1H), 7.57 ppm (d, 2H), 8.60 ppm (d, 2H)].

2.3. Preparation of pyridine functionalized carbon nanotube

Pyridine-functionalized carbon nanotube was prepared by direct modification of carbon nanotube surface with silane agents (Kathi and Rhee, 2008). In a typical reaction, carboxylic acid modified carbon nanotube (1.0 g) was suspended in 50 mL of toluene by the aid of ultrasound waves. Then TPI (2.0 mL) was added and the mixture was refluxed for 24 h. The solid phase was separated from the solvent by filtration and washed 3 times with ethanol in order to remove any impurities and then dried at room temperature. Formation of pyridine-functionalized carbon nanotubes was confirmed by IR spectroscopy, thermal analysis, scanning electron microscopy (SEM) and elemental analyses.

2.4. Apparatus

An AA-680 Shimadzu (Kyoto, Japan) flame atomic absorption spectrometer with a lead hollow cathode lamp at wavelength 283.3 nm resonance line and the spectral band pass at 0.5 nm was used. All measurements were carried out in an air/acetylene flame. Fourier-transform Infrared (FT-IR) spectra were recorded on a Bruker IFS66/S FT-IR spectrometer in KBr matrix. A digital pH meter, WTW Metrohm 827 Ion analyzer (Herisau, Switzerland), equipped with a combined glass calomel electrode was used for the pH adjustments at $25 \pm 1^\circ\text{C}$. The thermal analysis was performed using a BAHRTHERMO-analyse GmbH (Germany) employing heating at rates of $10^\circ\text{C min}^{-1}$ in air atmosphere. The elemental analyses (CHN) were performed on a Thermo Finnigan Flash-1112EA micro-analyzer. Morphology and size of the synthesized particles were observed on a Philips (XL-30, Almelo, Netherlands) scanning electron microscope (SEM) instrument.

2.5. Column preparation

For preparation of analysis column, 200 mg of pyridine-functionalized carbon nanotube was packed in a glass column with dimensions of 120 mm in length and 20 mm in diameter, and blocked by two polypropylene filters at the ends to prevent the loss of the modified MWCNT during sample loading. Prior to extraction, the column was preconditioned successively with 5 mL of absolute ethanol, 5 mL of toluene, 5 mL of absolute ethanol, and then washed with double-distilled water until it became free of organic solvents. The column was preconditioned by passing $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$ buffer solution with optimized pH (pH = 7.0).

2.6. Extraction procedure

The extraction procedure includes two steps: Adsorption and desorption. In the adsorption step, pH of sample solution was adjusted at pH = 7 (the optimum pH), then it was passed through the column at a flow rate of 24 mL min^{-1} using a peristaltic pump. The adsorbed lead ions were eluted from the column with 7 mL of 1 mol L^{-1} thiourea in 0.1 mol L^{-1} HCl solution at the flow rate of 4 mL min^{-1} . Afterward, the Pb(II) ions in the eluent were determined by FAAS.

2.7. Sample collection and preparation

The presented method was applied for determination of lead ions in aqueous samples. The water samples were obtained from tap water (Tehran, Iran), river water (Chaloos, Iran) and sea water (Caspian Sea). The water samples were collected in cleaned polyethylene bottles and were filtered through a $0.45 \mu\text{m}$ pore size nylon filter (Millipore) immediately after sampling. Two standard materials (NIST 1571 (Orchard leaves) and NIST 1572 (Citrus leaves)) with a certified amount of lead ions have been used. These samples were digested in an 8 mL mixture of 5% aqua regia with the assistance of a microwave digestion system. Digestion was carried out for 2 min at 250 W, 2 min at 0 W, 6 min at 250 W, 5 min at 400 W and 8 min at 550 W, and the mixture was then vented for 8 min. The residue from this digestion was then diluted up to 50 mL with deionized water (Ebrahimzadeh et al., 2012).

3. Results and discussion

3.1. Sorbent characterization

The pyridine-functionalization carbon nanotube was synthesized according to the previous report by the aid of silane agents (Kathi and Rhee, 2008). A schematic diagram of the synthesis system in the present study is shown in Fig. 1. The formation of pyridine-functionalized carbon nanotubes was confirmed by IR spectroscopy, scanning electron microscopy, elemental and thermal analysis. The FT-IR spectrum of pyridine-functionalized carbon nanotubes showed stretching vibration bands of carbon nanotubes and TPI organosilane (1081 , 1537 , 1633 , 1719 , 2972 , 3028 and 3480 cm^{-1}) and confirmed the presence of pyridine groups on the nanotube. Elemental analysis of the pyridine-functionalization carbon nanotubes gave a pyridine concentration of 1.86 mmol g^{-1} .

The thermal stability of pyridine-functionalization carbon nanotube was investigated by TGA/DSC analysis. According to the TGA/DSC analysis, sorbent is stable up to 230°C and loses about 40% weight upon heating to 800°C . This is in good agreement with the elemental analysis results (Fig. 2). The loss of 10% weight up to 230°C could be attributed to the release of physically absorbed and chemically bound water molecules. The combustion of the $\text{CH}_2\text{CH}_2\text{CH}_2\text{-Py}$ part of pyridine-functionalized carbon nanotube caused loss of approximately 32% weight of sorbent. Finally, in order to show the structure of synthesized sorbent, the SEM micrograph of pyridine-functionalized MWCNT was recorded. As it can be seen in Fig. 3, the structure of multiwalled carbon nanotubes was preserved after modification with the silane agent.

3.2. Optimization of the adsorption conditions

Since the extraction of Pb(II) ions on sorbent is strongly affected by adsorption conditions such as sample pH, flow rate, etc., these parameters were optimized during this study.

3.2.1. Effect of solution's pH

Since the pH could change the structure of pyridine groups, which are the coordination sites of the sorbent, pH is one of the most controlling parameters for adsorption of lead ions. The effect of varying pH values on Pb(II) ions adsorption was investigated by adjusting the pH of 25 mL sample solutions containing 1 mg L^{-1} of lead in the range of pH = 2 to pH = 9 using appropriate buffer solution. After passing the sample solutions through the column at flow rate of 10 mL min^{-1} , the adsorbed Pb(II) ions were eluted with 7 mL of 1 mol L^{-1} thiourea in 0.1 mol L^{-1} HCl solution at the flow rate of 4 mL min^{-1} and the Pb(II) ions in the eluent were determined by FAAS. As it can be seen in Fig. 4, the best pH for Pb(II) adsorption was found to be 6.0–7.0. Since the most natural aqueous samples have a pH of 7, the pH = 7.0 was chosen as optimum pH for further experiments.

3.2.2. Effect of sample flow rate

To optimize the sample flow rate, 25 mL solutions of 1 mg L^{-1} lead ions were adjusted to pH of 7.0, and then passed through the column at flow rates in the range of $4\text{--}28 \text{ mL min}^{-1}$ with a peristaltic pump. After eluting the adsorbed ions by with 7 mL of 1 mol L^{-1} thiourea in 0.1 mol L^{-1} HCl solution at the flow rate of 4 mL min^{-1} , the Pb(II) ions concentration in the eluent were determined by FAAS. As the results in Fig. 5 demonstrate, sample flow rate variation in the ranges of $4\text{--}24 \text{ mL min}^{-1}$ had no effect on the retention of the Pb(II) ions on pyridine-functionalized carbon nanotube.

3.3. Optimization of the desorption conditions

The desorption steps depend on different parameters, including type, concentration, volume and flow rate of eluent, which needs to be optimized for a better method performance.

3.3.1. Effect of type, concentration and volume of eluent

For desorption of Pb(II) ions from the pyridine-functionalized nanotubes, series of acidic eluent solutions such as HCl,

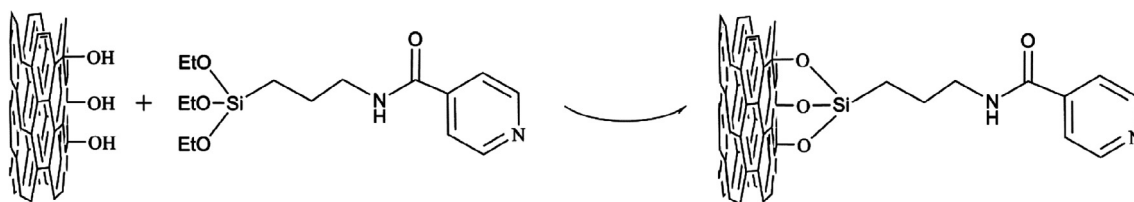


Figure 1 A schematic diagram for MWCNT modification.

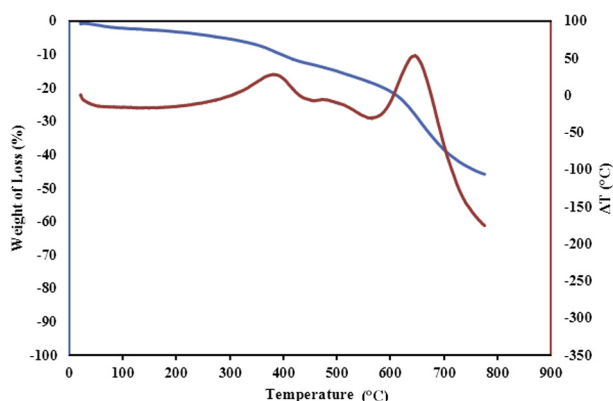


Figure 2 Thermal analysis of pyridine functionalized MWCNT.

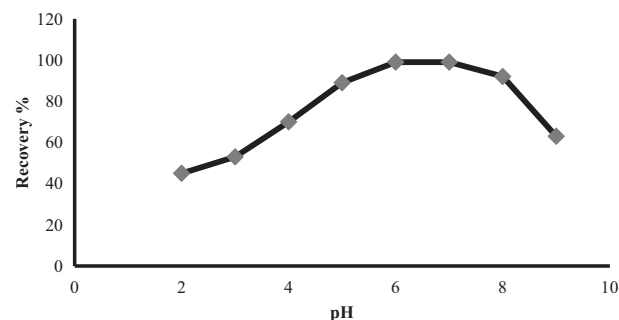


Figure 4 Effect of sample pH on the lead ions recovery using pyridine functionalized MWCNT.

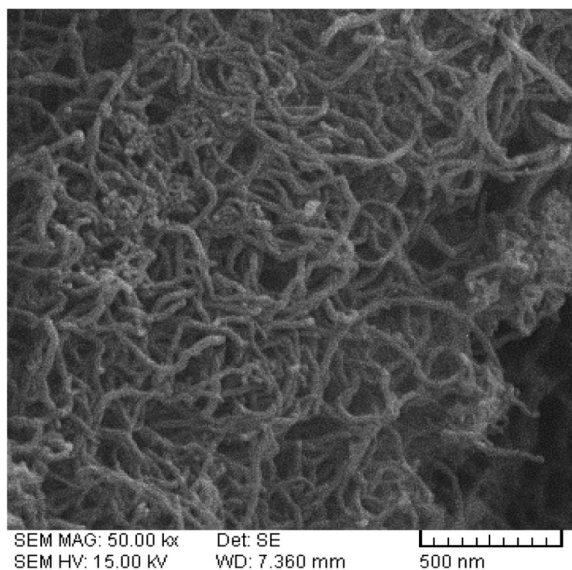


Figure 3 SEM micrograph of pyridine functionalized MWCNT.

HNO_3 , HClO_4 and H_2SO_4 and their mixture with thiourea, as a famous complexing agent in acidic media, were used. For this purpose, the pH of sample solution was adjusted at $\text{pH} = 7$ and it was passed through the column at a flow rate of 24 mL min^{-1} . The adsorbed lead ions were eluted from the column with different eluents and the Pb(II) ions in the eluents were determined by FAAS. As it is shown in Table 1, the best elution was performed by 1 mol L^{-1} thiourea in 0.1 mol L^{-1} HCl solution. Since the least volume of eluent is important for preconcentration factor (one of the important parameters for determination of SPE method efficiency) the volume of eluent should be optimized. To achieve the minimum volume of

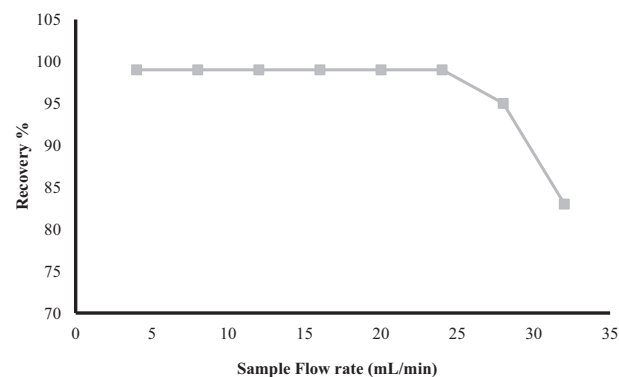


Figure 5 Effect of sample flow rate on the lead ions recovery using pyridine functionalized MWCNT.

Table 1 Effect of type, concentration and volume of eluent on recovery of gold ions.

Eluent	Volume (mL)	Concentration (mol L^{-1})	Recovery (%)
HCl	10	1	39.2
HNO_3	10	1	27.5
HClO_4	10	1	31.8
H_2SO_4	10	1	23.6
Thiourea + HCl	10	1/1	98.5
Thiourea + HCl	10	1/0.1	99.1
Thiourea + HCl	10	0.1/0.1	92.4
Thiourea + HCl	9	1/0.1	98.9
Thiourea + HCl	8	1/0.1	99.7
Thiourea + HCl	7	1/0.1	99.6
Thiourea + HCl	6	1/0.1	96.1

eluent, different volume of 1 mol L^{-1} thiourea in 0.1 mol L^{-1} HCl solution was tested as eluent and the results show that the recovery was reduced in the volumes less than 7 mL (Table 1).

3.3.2. Effect of eluent flow rate

To optimize the eluent flow rate, 25 mL solutions of 1 mg L^{-1} lead ions were adjusted to pH of 7.0, and then passed through the column at flow rates of 24 mL min^{-1} . The adsorbed ions were eluted by 7 mL of 1 mol L^{-1} thiourea in 0.1 mol L^{-1} HCl solution in different flow rates ranging from 1–10 mL min^{-1} . As the results in Fig. 6 demonstrate, the eluent flow rate could increase up to 4 mL min^{-1} with no decrease in elution efficiency.

3.4. Sorbent maximum capacity

The maximum adsorption capacity of the pyridine-functionalized multiwalled carbon nanotube with respect to Pb(II) ions was studied by passing 1000 mL portions of aqueous solutions

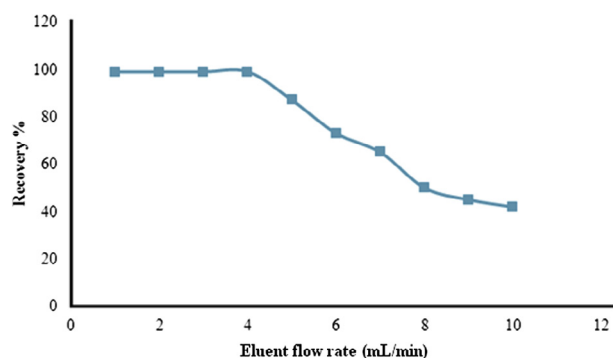


Figure 6 Effect of eluent flow rate on the lead ions recovery using pyridine functionalized MWCNT.

Table 2 The tolerance limit of diverse ions in the determination of lead ions.

Interfering ions	Tolerable concentration ratio X/Pb	Recovery (%)
Na ⁺	2000	98.7
K ⁺	2000	99.1
Ca ²⁺	1000	98.4
Mg ²⁺	1000	97.9
Zn ²⁺	500	96.8
Ni ²⁺	500	98.1
Co ²⁺	250	96.4
Fe ²⁺	250	95.7
Mn ²⁺	250	96.6
Hg ²⁺	250	97.3
Cr ³⁺	250	95.8
Ag ⁺	100	96.2

containing 200 mg of lead ions through the column at pH = 7.0, followed by its determination in the effluent and in the eluted solution using FAAS. The maximum capacity of this sorbent for three parallel works, was found to be $179 \pm 3 \text{ mg g}^{-1}$ (0.87 mmol g^{-1}) of Pb(II).

3.5. Effect of matrix ions

The effect of a variety of metal ions found in natural aqueous samples on the determination of Pb(II) ions was studied by adding various concentrations of different alkali metals, earth alkaline metals and some transition metals to 100 mL solutions containing 0.1 mg of Pb(II) ions. After applying the method, the amount of adsorbed lead ions was determined in the eluent. The tolerable amount was defined as the maximum concentration found to cause a change in signal that is less than 5% compared with the signal for lead alone. As shown in Table 2, the vast majority of metal ions do not interfere in preconcentration of Pb(II) ions on this sorbent, and the method is selective toward lead ions at pH = 7. The high selectivity of the sorbent to Pb(II) ions should be related to modification of the nanoparticles with the pyridine group as well as adsorption pH.

3.6. Figures of merit

In order to determine the limit of detection (LOD) of the presented method, a 500 mL blank solution ($n = 10$) was passed through the column under optimal experimental conditions. The value of limit of detection (LOD) for pyridine-functionalized multiwalled carbon nanotube was 2 ng mL^{-1} . These results were obtained from $C_{\text{LOD}} = 3S_b/m$. Also the precision of the method under optimum conditions was determined by performing ten replicates. The recovery value for lead ions was found to be 99.7% with a relative standard deviation of 1.3% on this sorbent.

3.7. Procedure validation studies

In order to investigate the accuracy of this method, several food reference materials containing a certified lead content was used. These samples were digested by the mentioned method and their Pb(II) concentrations were investigated by the presented method. As the results in Table 3 show, the pyridine-functionalized multiwalled carbon nanotube could be used as a confidential sorbent for extraction and determination of lead ions in natural samples.

3.8. Real samples analysis

The mentioned method was applied for the determination of lead ions concentration in aqueous samples. In this regard,

Table 3 Recovery for determination of lead in certified reference materials.

Sample	Unit	Concentration		Recovery (%)	RSD (%)
		Certified	Found ($n = 10$)		
NIST 1571 (Orchard leaves)	mg kg^{-1}	45.00	44.07	97.9	3.1
NIST 1572 (Citrus leaves)	mg kg^{-1}	13.30	12.79	96.1	2.7

Table 4 Results for the determination of lead content in aqueous samples.

Sample	Found (ng mL ⁻¹)	Added (ng mL ⁻¹)	C, found (ng mL ⁻¹ , <i>n</i> = 5)	Recovery (%)	RSD (%)
Distilled water	ND	20	19.9	99.5	1.3
Tap water	ND	20	19.8	99.0	1.9
River water	ND	20	20.3	101.5	2.4
Sea water	ND	20	19.5	97.5	2.7

Table 5 A comparison between this work and similar works.

Sorbent	LOD (ng mL ⁻¹)	RSD (%)	Recovery (%)	Ref.
Modified silica gel	7.5	2.7	95	Moghimini (2012)
Pb(II) ion imprinted polymers	0.20	2.0	95	Zhu et al. (2009)
Nano-silver coated silica gel	3.6	10	95	Baysal et al. (2009)
Modified activated carbon	0.43	2.1	99.3–101.6	Tian et al. (2010)
Polystyrene-divinylbenzene	25.0	2.1	97.5	Dutta and Das (2007)
Pyridine-MWCNT	2.0	1.3	99.7	This work

after sample preparation by the procedure mentioned above, the sample solution was adjusted to pH = 7 and then the amount of lead ions was determined in eluent by flame atomic adsorption spectroscopy after preconcentration by pyridine-functionalized MWCNT. As the results in Table 4 show, this method can be considered to be a reliable and fast method for Pb(II) determination in an aqueous sample. Table 5 shows a comparison between established method and recent published methods. As it can be seen in this table, the current method has lower DL in comparison to common methods. Although in some cases this method has higher DL, the advantages of this method are lower RSD and higher recovery.

3.9. Reusability

The long-term stability of pyridine-functionalized MWCNT as sorbent was investigated by successive sorption and elution cycles of 100 mL sample solutions containing 1 mg L⁻¹ of lead at the optimum condition. Afterward, the adsorbed metal ions were eluted by 7 mL of 1 mol L⁻¹ thiourea in 0.1 mol L⁻¹ HCl solution. By monitoring the change in the recoveries of the extraction of lead ions the stability of the sorption was estimated to be twelve adsorption–desorption cycles.

4. Conclusion

A novel highly mechanical and thermal stable sorbent was achieved by modification of multiwalled carbon nanotube surface with the triethoxysilane agent. The sorbent was fully characterized by IR spectroscopy, thermal analysis, elemental analysis and also scanning electron microscopy. This composite was used as a selective sorbent for preconcentration of Pb(II) ions in aqueous samples in pH = 7.0. The accuracy of the obtained method was confirmed by various standard reference materials. Finally, this method was used for determination of Pb(II) ions in natural aqueous samples. The high selectivity toward lead ions in pH = 7, high recoverability and having high adsorption capacity are the advantages of this new sorbent.

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